



# Mercury in the Amazon basin: Human influence or natural geological pattern?



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## ABSTRACT

One of the main scientific discussions on Hg levels in the Amazon region concerns the possible sources of this element. This research was conducted between 1999 and 2015 in the region between the coastal zone and the Amazonian Continental Shelf (ACS). The total Hg concentration values found in the sediments in ACS ranged from 14 to 160 ng g<sup>-1</sup>. The main contribution of metallic elements to ACS comes from the sedimentary load transported by the Amazon River basin. Among the main tributaries of the Amazon River, the Negro River, which for decades has had mining activity, and the Madeira River, which is still present today, although currently in decline. The analysis of the total Hg results associated with the suspended solids load, both in the Continental Amazon and ACS, suggest that the anthropogenic influence, although evident in sites sources of pollution, is not the main source of total Hg for ACS, and in this case the participation of the natural contributions should be attributed from the natural geological activity in the regional soil, which is considered as naturally enriched in Hg.

## 1. Introduction

The discussion if the main source of mercury (Hg) contamination is natural or anthropogenic in Amazon is classic and longstanding. Anyway, the sum of these two sources resulting in an immense volume of Hg, which partly is carried by the current flow associated with suspended sediments, towards the mouth of the Amazon River following the sedimentation process.

As a part of gold mining activities in Amazonia, Hg is used to form the amalgam and after that the liberation to atmosphere is estimated in up to 80%, the remaining is liberate to soil and rivers during the different phases of the gold extraction (Lacerda and Pfeiffer, 1992). The Hg in atmosphere has a short residence time and is deposited still near the source. The interaction of the metal forms in aquatic environment depend on the chemical forms and the physical and chemical properties of the water and commonly the metallic Hg present low mobility due to its association with the sediment and favoring the sedimentation. In the bottom, the biological metilation is encouraged, and the organic forms occur. The dissolved forms showed smaller importance in relationship the particulate forms in river environment overall in function of the solubility properties. Lacerda and Pfeiffer (1992) mentioned that

Amazonian rivers not influenced by mining activities show concentrations between 0.02 and 0.1 µg g<sup>-1</sup>, while in contaminated rivers, varied between 0.5 and 4.0 and could be reaching 19 µg g<sup>-1</sup>.

The natural composition of the Amazonian soil is considered enriched in Hg as explained by researchers in 90<sup>th</sup> decade (Roulet and Locotte, 1995), while attribute this richness to iron complex formed, process not so cleared and intensively discussed. This soil composition considered in large scale could contribute to the natural Hg signals on the near continental shelf of Amazon. Added to it, the consideration of the transport associated to suspended particulate matter is the way to reach long distances, for example the inner platform, from the without effective record in the bottom rivers, those not found important concentration in the river sediment.

The consideration of the both sources i.e. natural and anthropogenic of Hg transported by the Amazon river that represent about 18% of the world fluvial discharge (average ~180 000 m<sup>3</sup> s<sup>-1</sup>) (Goulding et al., 2003) with elevated solid suspended matter associated, about ~1.2 × 10<sup>9</sup> t year<sup>-1</sup> (Meade et al., 1985; Nittrouer et al., 1995), once reaching the continental platform will submitted to a coastal dynamic, mainly the influence of northwestward flowing North Brazilian Current along the American continent toward the Caribbean Seathe upper layer

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(Bourlès et al., 1999; Oudot et al., 1999). Associated to the river discharge, the suspended particulate matter receives the upper oceanic circulation influence on the material deposition on the shallow continental shelf.

The sediments that reach the Amazon Continental Shelf (ACS) from the Amazon River basin are formed by muddy material rich in organic matter, which is eventually deposited mainly in the inner part of the shelf due to the strength of the ocean (Siqueira et al., 2004; Siqueira and Aprile, 2012; Siqueira et al., 2016). This characteristic of the environment in to accumulate finer sediments in the inner shelf has important consequences for the complexation of metals, especially Hg. Aspects such as mobility and bioaccumulation of the metallic elements are directly associated with the chemical conditions, especially pH and oxy-reduction potential of the solution, and associated load of silt and silty-clay sediments with organic matter. In this way, the fluvial regime of the Amazon River basin, which influences marginal erosive processes, is a drive force for the variation of the metals concentration in the waters and sediments. In the case of Hg, this natural drive force is added to the anthropic activity, especially mining, representative in several tributaries of the Amazon River basin, citing Madeira, Tapajós and Trombetas rivers and their respective tributaries.

This research aimed to identify and to discuss the routes of Hg deposition, and to quantify the content of the total metallic element in different types of sediments present on the ACS adjacent coastal zone for the period monitored (1999–2015).

## 2. Material and methods

### 2.1. Study area

The study was conducted in the Amazon Continental Shelf (ACS) and nearby coastal zone (47°52'W–4°19'N and 51°04'W–2°16'S) between Orange Cape (State of Amapá) and Pará River mouth (State of Pará, Fig. 1). It is a region dynamic, conditioned by the meeting of continental waters with the Atlantic Ocean on influence at the Equatorial North Current and North Brazil Current (NBC). There is also interference from atmospheric forces as the Intertropical Convergence Zone, generating trade winds and rainfall, which determining the climatic seasons and the hydrological pattern of Amazonian rivers. According to Köppen-Geiger classification the climate of the region is "Am" hot and constantly humid (monsoon climate) for Marajó Bay, and "Af" equatorial for Amazon and Pará mouths, with a mean temperature of 28 °C and rainfall exceeding 2000 mm year<sup>-1</sup>, especially between the months of December and February (Siqueira and Aprile, 2012).

### 2.2. Analytical proceedings

Samples of 500 g of superficial sediments (0.0–0.1 m) were obtained with "van-Veen" collector at 25 sampling sites between 5 and 100 m isobaths during the months of lowest flow (May and June) in the Amazon River for the years 1999–2002, 2005–2007, 2011 and 2015, totaling 141 samples analyzed (all in triplicates). After sampling, sediments were stored in plastic bag in freezer at –20 °C until the analysis. At chemistry laboratory at the UFPA, the samples were dried at 45 °C for a period of 48 h, homogenized, sieved and pulverized, and the very fine sand fraction (125–63vfs μm) was used to determine organic matter (OM) and total Hg concentrations. Grain-size analysis was determined by the gravimetric method using sodium hexametaphosphate solution. The sand fractions (2000vcs – 63vfs μm) were obtained by sieving with water jet, the clay fraction (< 4 μm) was determined in a test tube for the separation of suspended material (Donagem et al., 2011), and silt was determined by mass difference. The OM was determined by hot acidic extraction, using 1.0 g of sediment sample with excess hydrogen peroxide (30%) on heater plate at 100 °C followed by drying the material in incubator at 60 °C, and by calculating the weight difference before and after dry digestion, with the results expressed as

percentages (%).

Total mercury was determined by the cold-vapor atomic absorption method (Standard Method 3112B and 3500-HgB -APHA, 2012) modified, adding 1.0 g of dry sediment sample (< 0.063 mm), 0.1 g of V<sub>2</sub>O<sub>5</sub>, 10 ml of HCl:HNO<sub>3</sub> 3:1 and 15 ml of H<sub>2</sub>SO<sub>4</sub> in a test tube closed to preserve and to promote recycling of the volatilized fumes. The material was heated at 80 °C for 60 min. After, the samples were transferred to a 100 ml volumetric flask and completed to volume with deionized water (Milli-Q). Aliquots were removed from the flasks for reading on atomic absorption spectrometer with cold-vapor generation and detection limit of 10 ng g<sup>-1</sup> (10 ppb) at the Lakefield Geosol Laboratories LTDA (MG). The results were certified from international standards MAG-1 Geostandards Newsletter and NIST 1646a, and were expressed in ng g<sup>-1</sup>.

### 2.3. Reference values and calculus

The choice of the most appropriate reference value (RV) for the application of environmental indicators is a constant discussion, and will be addressed in this research. Considering the diversity of the environment at the ACS, especially in relation to the origin of the oceanic sedimentation load, this study established the comparative use of Upper Continental Crust (UCC) as global reference values, established by Wedepohl (1995) and Rudnick and Gao (2003) compared to values described by Mason (1971). The medium shale was used as RV for interpreting data, while was of 56 ng g<sup>-1</sup> (Bowen, 1979).

Mercury levels were compared to sediment quality guideline values (SQGs), based on empirical values obtained from studies relating the concentration of toxic substances (organic and inorganic) to multiple toxicity tests in Canada and the USA. The SQGs were initially applied in the 1980s, having been reviewed and established by USEPA (1992), MacDonald et al. (1996), Canadian Council of Ministers of the Environment (CCME, 1999), and Chapman et al. (1999). These are guideline values used as a guide for toxicity to benthic biota, especially considering the bioavailability of metallic ions, and can be applied and compared in different aquatic environments (Long et al., 2005).

Using the Al element (Selvaraj et al., 2004) as RV and Hg as estimated metal content, the following calculations were applied: 1) Enrichment Factor (EF) defined by Gresens (1967), which represents the relationship between the abundance of a metallic element in the marine sediments (sample) and its natural abundance (background) in the rocks (equation (1)); 2) Potential Contamination Index (Cp) defined by Davault and Rognerud (2001), which relates the maximum concentration of a metal in the sample with its natural evidence (equation (2)); 3) Geoaccumulation Index (I<sub>Geo</sub>) of Müller (1969), calculated to evaluate the contamination of the environment by metallic elements (equation (3)); 4) SQGs - Threshold Effect Level (TEL) and Probable Effect Level (PEL) based on the limits established by MacDonald et al. (1996) and CCME (2014), and by the critical environmental levels described in CONAMA Resolution N°344 (BRASIL, 2004).

The data were normalized to the textural characteristic of sediments based on the concentration levels of Al, whose the capacity conservative has been proved efficient in aquatic environments (Selvaraj et al., 2004; Aprile and Bouvy, 2010), particularly in marine environments (Schiff and Weisberg, 1999). To test the influence of the fluvial discharge on the distribution and deposition of Hg the geochemical variables were combined in the form of axis of a principal component analysis (PCA).

$$EF = [Hg]_{sed}/[Al]_{sed}/[Hg]_{RV}/[Al]_{RV} \quad (1)$$

$$C_p = [Metal]_{max}/[Metal]_{RV} \quad (2)$$

$$I_{Geo} = \log_2 ([Metal]_{sed}/1.5 \times [Metal]_{RV}) \quad (3)$$

where RV is the background geochemical value in uncontaminated area (UCC).

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